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Citation: Journal of Agricultural and Food Chemistry (2003) 51: (3) 773-776

Number: 7186

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Drying Kinetics of Calcium Caseinate

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Drying is a major component of the cost of making caseinate-based films. We determined the drying curves for making calcium caseinate/glycerol films at low and high relative humidity at 21–34 °C. The drying curves exhibited a very long constant rate period followed by a single falling rate period. Much of the drying was in the constant rate period and preceded the actual film formation. Normally, calcium caseinate solutions are dried from about 5% solids, but it was possible to start with a more concentrated solution, 10% solids, to avoid much of the constant rate period. The resulting films were equal to those prepared starting at high initial moisture. An estimate of the drying costs indicated it is much cheaper to start with the more concentrated solutions.

KEYWORDS: Casein; film; coating; drying curve

INTRODUCTION

Tomasula et al. (1, 2) developed a continuous pilot plant process to produce casein with some of its micellar calcium intact and no added salts of neutralization. The process uses high-pressure CO₂ to reduce the pH to precipitate casein. When the pressure is removed, the CO₂ is vented and the pH returns to near the pH of milk. No salts of neutralization are present because there is no mineral acid present that needs neutralization.

The somewhat intact micellar casein presents the possibility of producing biodegradable polymer coatings with unique physical properties (3). They compared films made from high-pressure CO₂ with films made from calcium caseinate. CO₂-casein films were barely soluble and were slightly stronger and stiffer than corresponding calcium caseinate films. Glycerol (GLY) was the plasticizer in all cases.

They made the films in Petri dishes and dried the film solutions in ambient air. The "laboratory" Petri dish procedure takes about 1–2 days to make films at room temperature. We want to develop a process that is short enough that it can be run continuous on a pilot plant scale and ultimately develop a commercially feasible continuous process to make continuous polymer coatings. The first step is to determine the process kinetics for making casein-based films. Chen stated, "Little is known of the molecular mechanisms of the processes forming film" (4). However, the drying process can be elucidated. This is the determination of the drying curves that control the film-forming process.

Ideally, CO₂-casein would be used in these studies, but it is still a research material available in limited quantity. However, calcium caseinate is commercially available and should provide a suitable surrogate to determine the drying kinetics.

The objectives of this study are to determine the drying curves for calcium caseinate, to determine at what solids the film starts

to form, to determine if the drying curve changes when the film starts to form, and to establish feasible process parameters for a continuous process for making calcium caseinate films.

EXPERIMENTAL PROCEDURES

The raw materials were a commercial calcium caseinate, Alanate 310, NZMP(North America) Inc., and glycerol, 99.5% ACS reagent grade, Aldrich. The solvent was deionized water.

The calcium caseinate and glycerol were thoroughly mixed in the water with a Braun handblender, MR310, Braun Inc., Lynnfield, MA for 2 min or more. The solutions were refrigerated at least overnight to permit foam to disappear. In a continuous process, the foam would be removed, probably under vacuum. The solutions were dispensed into 100 × 15-mm Petri dishes by weight.

There were three general groups of solutions, 4–6% solids, 10% solids, and 15% solids (S/W + S). To achieve equal solids content in the finished films, different amounts of solution were added to the Petri dishes depending on the initial solids content. Namely, 20 g were used for the 6% solids solutions, 12 g were used for the 10% solids solutions, and 8 g for 15% solids solutions. Glycerol was included in the solids usually at the 30% level but, to see the effect of glycerol on film formation, was also included at 25 and 35% of the solids in some experiments. This way, the resulting film should be the same thickness and readily compared with physical tests and the cost of the films based on the amount of casein would be equal. The nominal mean film thickness in this study was 0.17 mm (SD = 0.041; *n* = 40).

Drying curves were obtained under conditions of natural convection in a very warm laboratory during the summer when the room was at 33–35 °C and >50% relative humidity. Films were also made under natural convection in the pilot plant. The relative humidity was ambient and uncontrolled. The pilot plant temperature ranged from 21 to 25 °C and relative humidity depended on the season of the year, ranging from 21 to 56%. Some films were made in a forced air convection oven (0.45 m/s) at 34 °C. The relative humidity was 21–25%.

Petri dishes containing solution were weighed at time 0 and then as a function of time. Curves of solution weight versus time of drying were determined. In experiments where the drying took more than 10 h, samples were started as early as possible on the first day and a second

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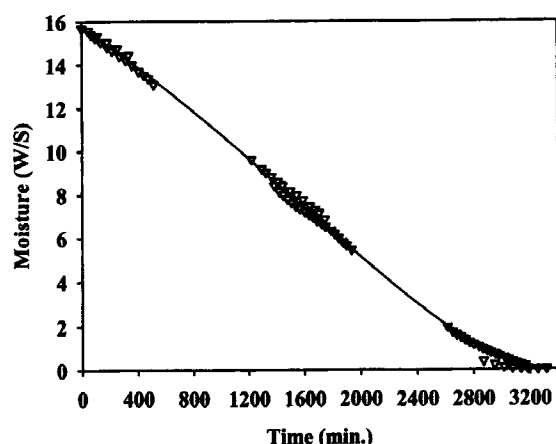


Figure 1. Calcium caseinate drying curve, 6% initial solids, 25% GLY, 23 °C, 51–62% H.

set started as late as possible on the first day. Data collection was suspended overnight but continued the next day. Drying on sequential days gave gaps in the curves. It is common practice in the drying industry to extrapolate the curves to the point of intersection and estimate the overall drying curve. After extrapolation, these data were then combined into one plot. Because the data were collected on different days, the relative humidity and temperature were slightly different and the two curves did not form a single continuous curve.

The Color Sphere Color System, BYK-Gardner, Inc., Silver Spring, MD was used to experimentally determine the point of film formation by monitoring the change in the transparency of the solutions during drying. The meter was calibrated using black and white standard tiles and a 2.5 cm port/viewing area.

The SensaDyne 6000 surface tension instrument (SensaDyne Instrument Division, Milwaukee, WI) was used to experimentally determine the surface tension of the starting solutions using the maximum bubble pressure method.

A null hypothesis (H_0 : $\text{mean}_1 = \text{mean}_2$) to compare the mean film thickness, tensile strength, and elongation at break.

RESULTS AND DISCUSSION

Drying Kinetics. The driving force or gradient in constant rate drying is the humidity ratio between the product or solution surface, which is saturated during constant rate drying, and the surrounding air (drying condition). The difference in humidity ratio at the solution surface to the air is proportional to the moisture removal rate from the surface and inversely proportional to the time of constant rate drying. The energy of the air (temperature) supplies the energy to drive the moisture from the solution. Air flow is used to maintain a constant humidity gradient or ratio. During a falling rate period, relative humidity relates to the solution water activity that relates to the solution equilibrium moisture content. The thickness or quantity of solution also affects the time needed to finish the drying (6).

Figure 1 presents an experimental drying curve for a calcium caseinate/glycerol (GLY) solution at room temperature (22–25 °C) and high ambient relative humidity (62%) using natural convection. The starting total solids concentration was 6% with 25% GLY. The drying curve was plotted as moisture content per total solids (W/S). There was a constant rate period lasting until about 0.40–0.35 solids. This was determined from the change in slope of the drying curve (W/S). This curve was a straight line, indicating the constant rate zone, until about 1.4 moisture (W/S). The constant rate period ends and the falling rate period begins about 1.4 (W/S) moisture as indicated by a gentle curve. There is no apparent second falling rate period as indicated by another change in the drying curve. The second

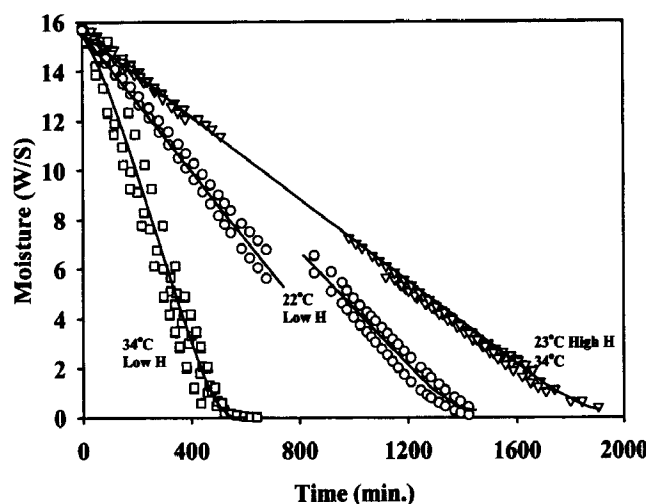


Figure 2. Calcium caseinate drying curves as a function of temperature and relative humidity, 6% initial solids, 30% GLY; 34 °C, high relative humidity (48–56%), natural convection; 23 °C, high relative humidity (48–56%), natural convection; 23 °C, low relative humidity (14–23%), natural convection; 34 °C, low relative humidity (14–23%), forced convection (0.1 m/s).

falling rate period would be caused by a change in drying diffusion mechanism. However, because the films are so thin, the second falling rate period appears to be nonexistent.

Figure 2 is a plot of drying curves at low relative humidity (21–23% H) and high relative humidity (48–56% H) plus low (23 °C) and elevated temperatures (34 °C). All curves were at natural convection except low relative humidity and 34 °C that was at forced convection. The initial solids content for the solutions was 6% and the glycerol was 30% of the solids. There was no noticeable difference in the drying curves between 25, 30, and 35% glycerol but the film properties were better at 30% (3). The drying curves were plotted as in Figure 1. The high temperature was chosen as 34 °C so when the process is ultimately applied to CO₂ separated casein there would be no thermal damage of proteins. A constant rate and falling rate period were found at low temperature and high relative humidity. As expected, there was no second falling rate period. The change in slope indicating the change to the falling rate period occurred between 0.4 and 0.3 solids. There was little difference in drying time because of temperature.

Relative humidity and air flow had a profound effect on the drying time. Whereas it took over 30 h to dry from 6% to 70% solids at high relative humidity, it took less than 9 h at low relative humidity, 34 °C, and forced convection. At low relative humidity, 34 °C, and forced convection it was difficult to determine when the constant rate period ended and the falling rate period began. However, the curves were similar to those at high relative humidity just with steeper slopes and more data scatter. The obvious conclusion is the solutions should be dried at low relative humidity, 34 °C, and forced convection to reduce the drying time.

Most of the drying time took place during the constant rate period from 6% solids to about 35% solids. We should be able to save time and money if we start with a more concentrated solution than 6% solids and dry the solutions at low relative humidity and forced convection. Obviously, using elevated temperature could further shorten the drying time; however, the ultimate goal is to make films using the undenatured CO₂ separated casein and fractions. Drying above 35 °C would cause some denaturation.

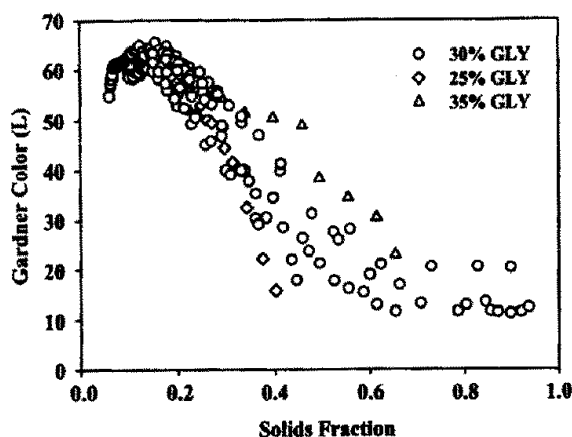


Figure 3. Determination of film initiation by Gardner Color, L as a function of solids content. Initial solids = S_0 .

During the drying process, the solutions turned from milky white and opaque to clear and transparent. The change apparently corresponds to film formation. Although this was visually discernible, exactly when the solutions start to become clear and transparent was subjective. However, all solutions visually appeared to start becoming transparent by about 23% solids. This would place film initiation somewhere in the falling rate period.

The human eye probably detects the visual change in the solution somewhat after the onset of film formation. An instrumental method should be more objective and sensitive for detecting the initiation of film formation. Therefore, we monitored the Gardner color of the solutions measuring the L-value (brightness), a-value (redness), or b-value (yellowiness) in the Petri dishes. Figure 3 plots the Gardner color brightness or transparency value, L, versus the solids content with different initial solids concentrations, 6, 10, and 15%. Three levels of glycerol (GLY), 25, 30, and 35% were included to determine if GLY shifted the results. In each case, there was a sharp drop in L-value a little before the visual observation of film formation. The plots in Figure 3 indicate the films start to form at about 15% solids as opposed to 23% observed visually. GLY content did not affect the results. The values for the Gardner color values, a and b, were also plotted (data not shown). The Gardner color a-value approximated a straight line with a very shallow positive slope. The b-values exhibited minima at 33% solids for 25 and 30% GLY. At 35% GLY, the b-value had a minima at 62–50% solids. On the basis of the Gardner L-values, we conclude the films start to form at 15% solids. Consequently, the initial solution solids concentration must be about 15% or less.

Figures 1 and 2 can be used to determine if film formation affects the drying rate evidenced by a change in drying rate at film formation. Calcium caseinate films start to form at solids content of 15% that is equal to 5.67 moisture, dry basis (W/S). At the dry weight basis moisture of 5.67, the slope of the drying curves in Figures 1 and 2 remain linear. There is no change in the slope in the drying curve. Hence, there is no effect on drying because of the start of film formation.

To compare the cost of drying casein films, a cost sensitivity study was made as a function of initial solids content. Because it is very early in the process development, the costs were calculated for comparison, not hard cost figures. These will have to wait for a continuous pilot plant process to be developed. Calculations were performed on the cost of removing the water from the film in a steam tube dryer on the basis of 1.5 kg of steam required to remove 1.0 kg of water. The steam costs were

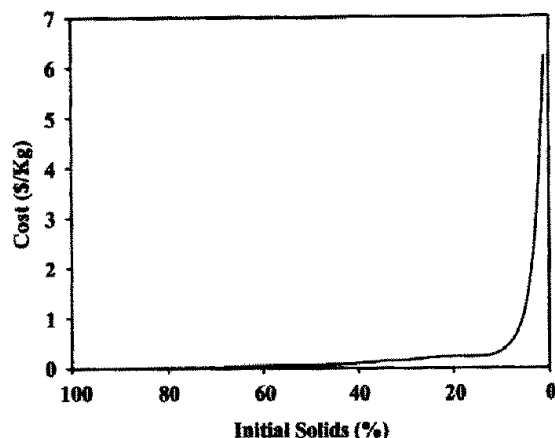


Figure 4. Drying cost, \$/kg, as a function of initial solids content.

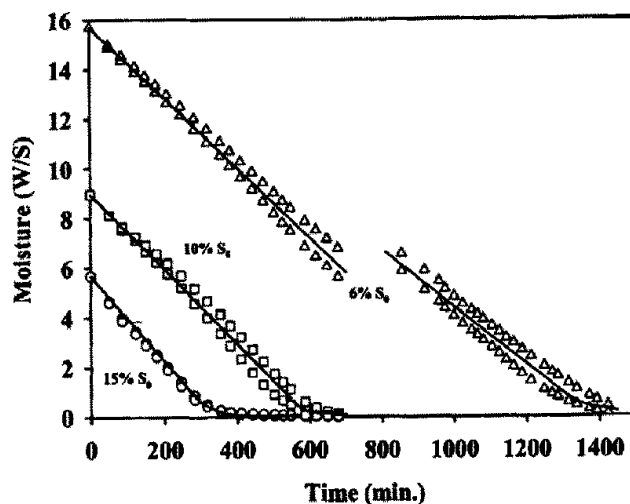


Figure 5. Calcium caseinate drying curves as a function of initial solids, S_0 .

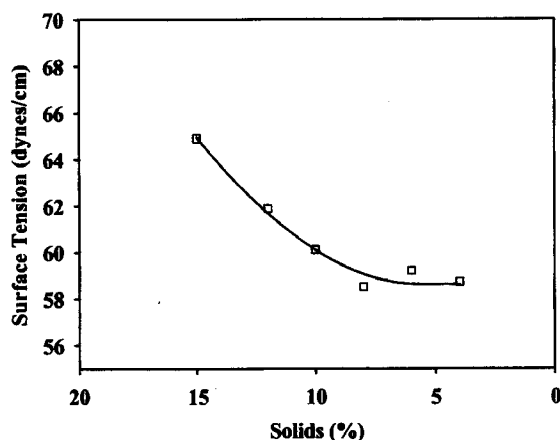
estimated at \$22.00 per thousand kg and the other drying costs (equipment, labor, electricity, etc.) were assumed to be equal to cost of the steam. Not surprisingly, the cost of drying increased with the volume of water being removed, Figure 4. For a film with a final 95% solids content, the drying costs were determined to be \$6.22 per kg of film produced with an initial 1% solids content. In films with an initial solids content of 10%, this cost dropped to \$0.56 per kg and for a 20% initial solids solution the costs were \$0.25 per kg of film. The drying costs for a 0.23-mm film translate to \$0.26/m² starting with a 10% initial solids concentration.

Drying curves were then determined starting with 6, 10, and 15% solids to see if it is possible to skip most of the constant rate drying period, from about 6% solids to 15% solids, and to compare the physical properties of the resulting films. These drying curves, Figure 5, indicate that we should be able to make casein films starting with 15–10% solids solutions. This is only true if the physical properties of the films are equal to or better than the films formed at lower temperatures starting with dilute solutions. Table 1 lists the physical properties of the films. Making a null hypothesis between means, there was no statistically significant difference in film thickness, tensile strength, or elongation at break for any of the three films. However, starting at 15% solids, the films started to form almost immediately. Also, the film solution was difficult to transfer without inserting air bubbles. The air bubbles did not break, even under vacuum. Although the films were of comparable physical properties, they always had defects when dried from 15% solids that would make the films unacceptable.

Table 1. Physical Properties of Films Made from 94, 90, and 85% Initial Moisture

initial solids	number of samples	film thickness mm	tensile strength (MPa)	elongation at break %	Young's modulus MPa
6%	5	0.236 (0.0342)	2.89 (0.530)	50.83 (12.290)	28.15 (8.379)
10%	5	0.234 (0.0356)	3.05 (0.342)	70.35** (4.098)	29.05 (6.569)
15%	5	0.229 (0.0289)	3.20 (0.442)	42.61 (6.785)	42.10* (8.218)

Values in parentheses are standard deviation. Significant differences represented by * $p \leq 0.05$, ** $p \leq 0.01$.

**Figure 6.** Surface tension of calcium caseinate solutions as a function of solids content.

Surface tension is the tendency of liquids to minimize the surface area. It is characterized by the ability of an object denser than the liquid, such as a metal pin, to float on the liquid. We determined the surface tension of various solution concentrations from 4–15% solids. The data are plotted in **Figure 6**. The surface tension is constant from 4% to near 10% solids and then rises rapidly. On the basis of this plot and our experience making films from 15% solids solutions, we decided to use 10% solids solutions as the starting material. It affords a nice savings in drying costs yet permits easy film preparation.

The heat transfer coefficient can be calculated from the constant rate curves in **Figures 1, 2, and 5**. Equation 1 gives the heat transfer rate, Q

$$Q = m_c * H_L \quad (1)$$

where m_c is the evaporation rate and H_L is the latent heat of evaporation. The slope of the lines m_c and H_L can be found from the steam tables. The value of h can be calculated by substituting Q into eq 2

$$Q = h * A * (T_a - T_s) \quad (2)$$

where h is the heat transfer coefficient, A is the surface area of the film solution, T_a is the air temperature, and T_s is the temperature of the liquid surface. From **Figures 1, 2, and 5**, the average value for h was 0.0119 cal/min cm² °C with a standard deviation of 0.0054 ($n = 10$).

Experimentally, the equilibrium moisture of the films varied with the relative humidity. At 52% H, the equilibrium moisture was 0.0012 (W/S) and at 0% H, the equilibrium moisture was 0.0007 (W/S). These values are less than the experimental error in determining moisture. Therefore, the equilibrium moisture was assumed to be 0.0 in all data analyses.

CONCLUSIONS

Drying curve data provided the information to determine the drying kinetics of calcium caseinate/glycerol films. The bulk of the drying occurs in the constant rate region. Films formed from 6, 10, and 15% initial solids have similar physical properties. However, films formed from 15% initial solids solutions usually have defects. On the basis of the Gardner L-values, films start to form at 15% solids. There is no effect on drying because of the start of film formation. Surface tension of the starting solutions increases rapidly above 10% solids. Therefore, from an economic standpoint, it is best to make the calcium caseinate films starting with 10% initial solids, dry at low relative humidity at 34 °C, and forced convection. On the basis of these conclusions, the next step of the research will be to develop a continuous pilot plant process using 10% initial solids, low relative humidity, 34 °C, and forced convection.

ABBREVIATIONS

W, weight of water; S, weight of dry solids; H, relative humidity; Q , heat transfer rate; m_c , the evaporation rate; H_L , the latent heat of evaporation; h , the heat transfer coefficient; A , the surface area of the film solution; T_a , the air temperature; T_s , the temperature of the liquid surface

ACKNOWLEDGMENT

The authors thank David Coffin and John Mulherin who performed some of the physical properties tests.

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Received for review June 6, 2002. Revised manuscript received October 10, 2002. Accepted November 7, 2002.